

MS

VERIFICATION OF TRANSLATION

I, Melissa Stanford, a translator with Chillson Translating Service, 3530 Chas Drive, Hampstead, Maryland, 21074, hereby declare as follows:

That I am familiar with the French and English languages;

That I am capable of translating from French to English;

That the translation attached hereto is a true and accurate translation of French Application FR 00/04084 titled, "Process for Desulfurizing Gasoline Comprising A Desulfurization Of Heavy Fractions And Intermediate Fractions That Are Obtained From A Fractionation Into At Least Three Fractions;"

That all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true;

And further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any registration resulting therefrom.

By Melissa Stanford

Executed this 16 day of April 2003.

Witness Steve Chills

Translator's Note:

One or more words, namely at least one verb, are missing in the sentence beginning with
“Cette étape... [This stage]” on German page 15, line 11 (English page 21, line 11).

INPI

NATIONAL INSTITUTE OF INDUSTRIAL PROPERTY

PATENT

RECEIVED
APR 24 2001
TC 1700

CERTIFICATE OF DESIGN - CERTIFICATE OF ADDITION

OFFICIAL COPY

The General Director of the National Institute of Industrial Property certifies that the attached document is a certified true copy of an application for a certificate of industrial property that is filed with the Institute.

Done in Paris on FEBRUARY 27, 2001

For the General Director of the National
Institute of Industrial Property
Head of the Patent Department

/s/

Martine PLANCHE

INPI

NATIONAL INSTITUTE OF

INDUSTRIAL PROPERTY

26bis, rue de Saint Pétersbourg

75800 Paris Cédex 08

Telephone: 01 53 04 53 04

Fax: 01 42 94 86 54

Reserved for the INPI

DELIVERY OF THE DOCUMENTS

DATE

3/29/2000

LOCATION

99

NATIONAL REGISTRATION NO.

0004084

ATTRIBUTED BY THE INPI

FILING DATE ATTRIBUTED BY

MARCH 29, 2000

THE INPI

Your references for this file (optional) PC/CS

- 1 NAME AND ADDRESS OF THE APPLICANT OR THE AGENT TO WHOM THE
CORRESPONDENCE SHOULD BE SENT

INSTITUT FRANCAIS DU PETROLE

[FRENCH PETROLEUM INSTITUTE]

Patent Department

1 and 4 avenue Bois Préau

92852 RUEIL MALMAISON CEDEX

CERTIFICATE OF DESIGN No. 11354*01

Intellectual Property Code – Book VI

REQUEST FOR ISSUANCE 1/2

RECEIVED
APR 24 2000
TC 1700

This form must be filled out legibly in black ink

Confirmation of filing by fax

2 NATURE OF THE APPLICATION Check one of the 4 boxes below

Patent Application ☒ X

3 TITLE OF THE INVENTION (maximum of 200 characters or spaces)

PROCESS FOR DESULFURIZING GASOLINE COMPRISING A
DESULFURIZATION OF HEAVY FRACTIONS AND INTERMEDIATE FRACTIONS
THAT ARE OBTAINED FROM A FRACTIONATION INTO AT LEAST THREE
FRACTIONS

**4 DECLARATION OF PRIORITY OR REQUEST TO TAKE ADVANTAGE OF THE
FILING DATE OF A PRIOR FRENCH APPLICATION**

5 APPLICANT

Name or corporate name	INSTITUT FRANCAIS DU PETROLE		
First names			
Legal form	Professional entity		
SIREN No.			
APE-NAF code			
Address : Street	1 and 4 avenue Bois Préau		
Zip Code and City	92852	RUEIL MALMAISON CEDEX	
Country	FRANCE		
Nationality	FRENCH		
Telephone No. (optional)	01 47 52 62 84		
Fax No. (optional)	01 47 52 70 03		
E-mail (optional)			

INPI

PATENT

**NATIONAL INSTITUTE OF
INDUSTRIAL PROPERTY**

**CERTIFICATE OF DESIGN
REQUEST FOR ISSUANCE 2/2**

Reserved for the INPI

DELIVERY OF THE DOCUMENTS

DATE

3/29/2000

LOCATION

99

NATIONAL REGISTRATION NO.

0004084

ATTRIBUTED BY THE INPI

Your references for this file:

PC/CS

(optional)

6 AGENT

7 INVENTOR(S)

The inventors are the applicants

☒ No

In this case, provide a separate designation
of inventor(s)

8 SEARCH REPORT **Only for a patent application (including division and transformation)**

Immediate drawing-up ☒

9 REDUCTION OF THE FEE LEVEL

If you have used the "continuation" form,
indicate the number of attached pages

INSTITUT FRANÇAIS DU PÉTROLE

Patent Department

10 SIGNATURE OF THE APPLICANT OR AGENT SIGNATURE OF THE PRE-

(Name and Position of the Signatory)

FECTION OR THE INPI

/s/

/s/

FRANÇOIS ANDREEFF

Chief Engineer

Law No. 78-17 of January 6, 1978 pertaining to data-processing, to files and to rights applies to responses made on this form. It guarantees the right to access and correct the information that applies to you at the INPI.

INPI

NATIONAL INSTITUTE OF

INDUSTRIAL PROPERTY

PATENT DEPARTMENT

26bis, rue de Saint-Pétersbourg

75800 Paris Cedex 08

Telephone: 01 53 04 53 04

Fax: 01 42 93 59 30

PATENT

CERTIFICATE OF DESIGN

Intellectual Property Code – Book VI

DESIGNATION OF INVENTOR(S)

Page No. 1../2..

(If the applicant is not the inventor or the sole
inventor)

This form is to be filled out legibly in black ink

cerfa

No. 11235*02

Your references for this file (optional)

PC/CS

NATIONAL REGISTRATION NO.

0004084

TITLE OF THE INVENTION (maximum of 200 characters or spaces)

PROCESS FOR DESULFURIZING GASOLINE COMPRISING A DESULFURIZATION
OF HEAVY FRACTIONS AND INTERMEDIATE FRACTIONS THAT ARE OBTAINED
FROM A FRACTIONATION INTO AT LEAST THREE FRACTIONS

THE APPLICANT(S):

INSTITUT FRANCAIS DU PETROLE

**DESIGNATE AS INVENTOR(S): (Indicate at top right “Page No. 1/1.” If there are more
than three inventors, use an identical form and number each page by indicating the
total number of pages.)**

Name DEBUISSCHERT
First Name Quentin
Address Street 12 allée de la Pagerie
Zip Code and City 92500 RUEIL MALMAISON
Company of affiliation (optional)

Name DIDILLON
First Name Blaise
Address Street 38 rue Emile AUGIER
Zip Code and City 92500 RUEIL MALMAISON
Company of affiliation (optional)

Name NOCCA
First Name Jean-Luc
Address Street 1714 Cottage Landing
Zip Code and City HOUSTON, TX 77077 USA
Company of affiliation (optional)

**DATE AND SIGNATURE(S)
OF THE APPLICANT(S) OR
THE AGENT**

**(Name and position of the
signatory)**

**INSTITUT FRANÇAIS DU PÉTROLE
PATENT DEPARTMENT**

/s/

**FRANÇOIS ANDREEFF
Chief Engineer**

Law No. 78-17 of January 6, 1978 pertaining to data-processing, to files and to rights applies to responses made on this form. It guarantees the right to access and correct the information that applies to you at the INPI.

INPI

NATIONAL INSTITUTE OF

INDUSTRIAL PROPERTY

PATENT DEPARTMENT

26bis, rue de Saint-Pétersbourg

75800 Paris Cédex 08

Telephone: 01 53 04 53 04

Fax: 01 42 93 59 30

PATENT

CERTIFICATE OF DESIGN

Intellectual Property Code – Book VI

DESIGNATION OF INVENTOR(S)

Page No. 2../2..

(If the applicant is not the inventor or the sole inventor)

This form is to be filled out legibly in black ink

cerfa

No. 11235*02

Your references for this file (optional)

PC/CS

NATIONAL REGISTRATION NO.

0004084

TITLE OF THE INVENTION (maximum of 200 characters or spaces)

PROCESS FOR DESULFURIZING GASOLINE COMPRISING A DESULFURIZATION
OF HEAVY FRACTIONS AND INTERMEDIATE FRACTIONS THAT ARE OBTAINED
FROM A FRACTIONATION INTO AT LEAST THREE FRACTIONS

THE APPLICANT(S):

INSTITUT FRANCAIS DU PETROLE

DESIGNATE AS INVENTOR(S): (Indicate at top right “Page No. 1/1.” If there are more than three inventors, use an identical form and number each page by indicating the total number of pages.)

Name UZIO
First Name Denis
Address Street 4 Square Saint Germain
Zip Code and City 78160 MARLY LE ROI
Company of affiliation (optional)

Name
First Name
Address Street
Zip Code and City
Company of affiliation (optional)

Name
First Name
Address Street
Zip Code and City HOUSTON, TX 77077 USA
Company of affiliation (optional)

**DATE AND SIGNATURE(S)
OF THE APPLICANT(S) OR
THE AGENT**

**(Name and position of the
signatory)**

INSTITUT FRANÇAIS DU PÉTROLE

PATENT DEPARTMENT

/s/

FRANÇOIS ANDREEFF

Chief Engineer

Law No. 78-17 of January 6, 1978 pertaining to data-processing, to files and to rights applies to responses made on this form. It guarantees the right to access and correct the information that applies to you at the INPI.

Prior Art:

The production of reformulated gasolines that meet the new environmental standards requires in particular that the olefin concentration be slightly decreased but that the concentration of aromatic compounds (primarily benzene) and sulfur be significantly decreased. The catalytic cracking gasolines, that can account for 30 to 50% of the gasoline pool, have high olefin and sulfur contents. The sulfur that is present in the reformulated gasolines can be nearly 90% attributed to catalytic cracking gasoline (FCC, "fluid catalytic cracking" or fluidized-bed catalytic cracking). The desulfurization (hydrodesulfurization) of gasolines and primarily FCC gasolines is therefore of obvious importance for meeting specifications. Besides catalytic cracking gasoline, other gasolines, such as the gasolines that are obtained directly from crude oil distillation or conversion product gasolines (coker, steam-cracking or the like) can contribute significantly to the sulfur in gasoline.

Hydrotreatment (hydrodesulfurization) of the feedstock that is sent to the catalytic cracking leads to gasolines that typically contain 100 ppm of sulfur. The units for hydrotreatment of catalytic cracking feedstocks operate, however, under rigorous temperature and pressure conditions that assume a high investment. In addition, the entire feedstock of the catalytic cracking process should be desulfurized, which brings about the treatment of very high volumes of feedstock.

Hydrotreatment (or hydrodesulfurization) of catalytic cracking gasolines, when it is carried out under standard conditions that are known to one skilled in the art, makes it possible to reduce the sulfur content of the fraction. This process, however, exhibits the major drawback of bringing about a very significant drop in the octane number of the fraction because of the saturation of a significant proportion of the olefins during hydrotreatment.

The separation of light gasoline and heavy gasoline before hydrotreatment was already claimed in Patent US-A- 4 397 739. This type of separation makes it possible to separate a light, olefin-rich fraction that has a low sulfur content that will no longer be compatible with future specifications and a rich heavy fraction that is low in olefins and that contains a large proportion of sulfur in the initial gasoline. In this patent, a process for hydrodesulfurization of the gasolines comprising a fractionation of the gasoline into a light fraction and a heavy fraction and a specific hydrodesulfurization of the heavy gasoline is claimed, but no solution for eliminating the sulfur that is present in the light gasoline is proposed.

In contrast, Patent US-A- 4 131 537 teaches the advantage of fractionating gasoline into several fractions, preferably three, based on their boiling point, and desulfurizing them under conditions that may be different and in the presence of a catalyst that comprises at least one metal of group VIB and/or group VIII. In this patent, it is indicated that the greatest benefit is obtained when the gasoline is fractionated into three fractions and when the fraction that has intermediate boiling points is treated under mild conditions.

Patent Application EP-A- 0 725 126 describes a process for hydrodesulfurization of a cracking gasoline in which the gasoline is separated into a number of fractions comprising at least a first fraction that is high in compounds that are easy to desulfurize and a second fraction that is high in compounds that are difficult to desulfurize. Before carrying out this separation, it is necessary first of all to determine the distribution of the sulfur-containing products by means of analyses. These analyses are necessary for selecting the equipment and the separation conditions.

In this application, it is thus indicated that the olefin content and the octane number of a

light cracking gasoline fraction drop significantly when it is desulfurized without being fractionated. In contrast, the fractionation of said light fraction into 7 to 20 fractions followed by analyses of sulfur and olefin contents of these fractions makes it possible to determine the fraction or fractions with the highest contents of sulfur-containing compounds that are then desulfurized simultaneously or separately and mixed with other fractions that may or may not be desulfurized. Such a procedure is complex and should be reproduced with each change in the composition of the gasoline to be treated.

French Patent Application No. 98/14480 teaches the advantage of fractionating the gasoline into a light fraction and a heavy fraction and then in carrying out a specific hydrotreatment of the light gasoline on a catalyst with a nickel base, and a hydrotreatment of the heavy gasoline on a catalyst that comprises at least one metal of group VIII and/or at least one metal of group VIb.

Also proposed, for example in Patent US-A-5 290 427, were processes for hydrotreatment of gasolines that consist in fractionating gasoline then in introducing fractions at different levels of a hydrodesulfurization reactor and in converting the desulfurized fractions on a zeolite ZSM-5 to offset by isomerization the octane loss that is noted.

In these processes, the gasolines that are to be treated in general have a starting point that is higher than 70°C, and there again it is necessary to treat the light gasoline separately (fraction corresponding to the compounds with a boiling point of between C5 (hydrocarbon with 5 carbon atoms) and 70°C) for example by a softening. Patent US-A-5 318 690 proposes a process that comprises a fractionation of the gasoline and a softening of the light gasoline, while the heavy gasoline is desulfurized and then converted to ZSM-5 and desulfurized again under mild

conditions. This technique is based on a separation of the crude gasoline so as to obtain a light fraction that is virtually lacking sulfur-containing compounds other than the mercaptans. This makes it possible to treat said fraction only with a softening that removes the mercaptans.

As a result, the heavy fraction contains a relatively large amount of olefins that are partly saturated during hydrotreatment. To compensate for the drop of the octane number linked to the hydrogenation of the olefins, the patent recommends cracking on the ZSM-5 zeolite that produces olefins, but to the detriment of the yield. In addition, these olefins can be recombined with the H_2S that is present in the medium to reform mercaptans. It is then necessary to carry out a softening or an additional hydrodesulfurization.

Summary of the Invention:

This invention relates to a process for desulfurizing gasoline, i.e., a process for the production of gasolines with a low sulfur content, which makes it possible to upgrade the entire feedstock (in general a gasoline fraction) that contains sulfur, preferably a gasoline fraction that is obtained from a catalytic cracking process, and to reduce the sulfur contents in said gasoline fraction to very low levels, without a significant reduction of the gasoline yield and while minimizing the reduction of the octane number due to the hydrogenation of the olefins. In addition, the process according to the invention makes it possible to restore at least in part the possible octane losses due to the hydrogenation of olefins via the reforming of one of the fractions of previously desulfurized gasolines.

The process according to the invention is a process for the production of gasoline with a low sulfur content from a feedstock that contains sulfur. It comprises at least the following

stages:

a1) At least a selective hydrogenation of diolefins and acetylenic compounds that are present in the feedstock,

a2) Optionally at least one stage whose purpose is to increase the molecular weight of light sulfur-containing products present in the feedstock or the effluent of stage a1.

This stage optionally can be carried out simultaneously to stage a1 on at least a portion of the feedstock, in the same reactor or in a different reactor. It can also be carried out separately on at least a portion of the hydrogenated feedstock in stage a1.

b) At least one separation (also called fractionation below) of the gasoline that is obtained in stage a1 or a2 into at least three fractions, whereby a light fraction contains the lightest olefins of the initial gasoline (light gasoline or light fraction), a heavy fraction in which the major portion of the sulfur-containing compounds that are initially present in the initial gasoline is concentrated (heavy gasoline or fraction), and whereby at least one intermediate fraction has relatively low olefin and aromatic compound contents and therefore a low octane number relative to the light and heavy fractions of this gasoline.

c1) At least one treatment of the heavy gasoline that is separated in stage b) on a catalyst that makes it possible to decompose or to hydrogenate at least partially the unsaturated sulfur-containing compounds, in particular the cyclic and even aromatic sulfur-containing compounds, such as, for example, the thiophene compounds, by placing them under conditions such that the hydrogenation of the olefins on this catalyst is limited. The heavy fraction optionally can be mixed before or after this stage c1, with at least a portion of an intermediate fraction that is obtained from stage b for separation and preferably non-desulfurized.

c2) Stage c1 is optionally followed by a stage c2 for treatment of the effluent of stage c1 on a catalyst that makes it possible to decompose the sulfur-containing compounds and more preferably the linear and/or cyclic saturated sulfur-containing compounds, with a limited hydrogenation of olefins.

d) At least one stage whose purpose is to lower significantly the sulfur and nitrogen contents of at least one of the intermediate fractions. This stage of desulfurization and denitration is preferably accompanied by a virtually total hydrogenation of the olefins that are present in this fraction. The fraction that is thus obtained is then treated by catalytic reforming so as to increase the octane number of said intermediate fraction(s).

e) Optionally a stage e for mixing at least two fractions of which at least one has undergone a desulfurization treatment in stage c1 and optionally c2 and/or in stage d.

The catalytic treatments of stages c1 and/or c2 can be carried out either in a single reactor that contains the two catalysts or in at least two different reactors. When the treatment is carried out with two reactors, the latter two are preferably placed in series, whereby the second reactor preferably integrally treats the effluent at the outlet of the first reactor, preferably without separating the liquid and the gas between the first and the second reactor. It is also possible to use several reactors in parallel or in series for one and/or the other of stages c1 or c2.

Furthermore, a stage e is preferably carried out after stage d, and this stage consists in mixing the separated gasolines in stage b that they may or may not have undergone desulfurization treatments.

The feedstock of the process according to the invention is generally a sulfur-containing gasoline fraction, such as, for example, a fraction that is obtained from a coking unit, a

visbreaking unit, a steam-cracking unit or a catalytic cracking unit (FCC). Said feedstock preferably consists of a gasoline fraction that is obtained from a catalytic cracking unit, whose range of boiling points typically extends from approximately the boiling points of the hydrocarbons with 5 carbon atoms (C_5) up to about 250°C . This gasoline optionally can consist of a significant gasoline fraction of other origins, such as the gasolines that are obtained directly from the atmospheric distillation of the crude oil (straight run gasoline) or the conversion process (coker or steam-cracking gasoline, for example). The end point of the gasoline fraction depends on the refinery from which it is obtained and market constraints, but generally remains in the limits indicated above.

Detailed Description of the Invention:

In this invention, a process is described that makes it possible to obtain a gasoline that contains sulfur-containing compounds, preferably obtained from a catalytic cracking unit, in which the gasoline first undergoes a selective hydrogenation treatment of diolefins and acetylenic compounds, then optionally a stage whose purpose is to increase the weight of the lightest sulfur-containing compounds, optionally present in the gasoline, and which should, lacking this stage, be found in the light gasoline after fractionation, at least a separation of the gasoline into at least three fractions, a treatment of at least one of the intermediate fractions whose purpose is to desulfurize and to denitrate this fraction significantly before subjecting it to a catalytic reforming treatment, a treatment of heavy gasoline that is optionally mixed with at least a portion of one of the intermediate fractions, with a catalyst that is known for promoting the transformation of unsaturated sulfur compounds that are present in gasoline, such as, for example, the thiophenic

compounds, into saturated sulfur compounds, such as thiophanes, mercaptans, then optionally a second catalyst that promotes the selective transformation of saturated sulfur compounds that are linear or cyclic and are already present in the heavy fraction or are produced during the preceding treatment. The thus treated heavy and intermediate fractions and optionally the light gasoline fraction can then be mixed so as to obtain a desulfurized gasoline.

This scheme makes it possible ultimately to obtain a desulfurized gasoline with a monitoring of the content of olefins or the octane number, even for the high desulfurization rates. Thanks to this process, high hydrodesulfurization rates are obtained under reasonable operating conditions that are specified below. In addition, by optimizing the fraction points of intermediate fractions and by selecting those that are sent to the catalytic reforming stage, it is possible to minimize the benzene content of the final gasoline (for example to contents that are less than 5% by weight in the final mixture of the desulfurized gasoline fractions), to control the olefin content, and to maintain the high research octane number and engine octane number values.

The sulfur-containing radicals contained in the feedstocks that are treated by the process of the invention can be mercaptans or heterocyclic compounds, such as, for example, thiophenes or alkyl-thiophenes, or heavier compounds, such as, for example, benzothiophene or dibenzothiophene. When the gasoline that contains light sulfur-containing compounds is fractionated into two fractions, a light fraction that is high in olefins and a heavy fraction that is low in olefins, the light sulfur-containing compounds (for example: ethyl mercaptan, propylmercaptan and optionally thiophene) can be partly, and optionally entirely, present in the light gasoline. It is often then necessary to apply an additional treatment to this light fraction to reduce the sulfur content that it contains. In a conventional manner, this treatment is, for

example, an extractive softening that makes it possible to eliminate from the gasoline the light sulfur compounds that are present in mercaptan form. In addition to the fact that this treatment inevitably increases the operational cost, it is operational only if the sulfur is in the form of mercaptan. The fractionation point of the gasoline should therefore preferably be limited so as not to entrain the presence of thiophene in the light gasoline. The latter actually forms azeotropes with a certain number of hydrocarbons; it will be possible to separate in the light gasoline only the C₅ olefins and a small portion of the C₆ olefins for fear of entraining too large a thiophene fraction into this fraction.

In the process according to the invention, to make it possible to recover a larger fraction of the olefins that are present in the light gasoline while limiting the sulfur content of this fraction without additional treatment, it is proposed in a preferred manner to treat the feedstock, after a first stage of selective hydrogenation, under conditions and on catalysts that make it possible to transform the light sulfur-containing compounds into sulfur-containing compounds with a higher boiling point so that they are found again after the separation stage in heavier fractions. The gasoline is then fractionated into at least three fractions: a light fraction that contains a significant fraction of the olefins that are initially present in the gasoline to be treated but a very small amount of sulfur-containing compounds, at least one intermediate fraction that is desulfurized and denitrated, then treated in a reforming catalyst, and a heavy fraction that is desulfurized under defined conditions and with a catalyst or a concatenation of catalysts making it possible to reach high desulfurization rates while limiting the hydrogenation rate of olefins and therefore the octane loss. To reduce the benzene content of the final gasoline, one of the more preferred embodiments of the invention consists in treating the feedstock under conditions and

on catalysts that make it possible to transform the light sulfur-containing compounds into sulfur-containing compounds with a higher boiling point found after the separation stage into heavier fractions. The gasoline is then separated into 4 fractions:

- A light fraction that contains the main fraction of molecules with 5 carbon atoms (C_5) and a significant fraction of molecules with 6 carbon atoms (C_6) that are initially present in the gasoline that is to be treated. This fraction is characterized by a significant concentration of olefins and a very low content of sulfur,
- A first intermediate fraction that essentially consists of (i.e., at more than 60% by weight, preferably more than 80% by weight) molecules with six carbon atoms (C_6) and a portion of the molecules that have 7 carbon atoms (C_7) as well as the largest portion of sulfur-containing compounds that have a boiling point that is close to that of the azeotrope that it forms with hydrocarbons, at about nearly 20%. This fraction is preferably mixed with heavy gasoline before hydrodesulfurization (stages c1 and c2) or after decomposition or at least partial hydrogenation of unsaturated sulfur-containing compounds (stage c1) but before decomposition of saturated sulfur-containing compounds (stage c2) so as to be desulfurized under conditions that make it possible to limit the hydrogenation of olefins. This gasoline is preferably not sent to the catalytic reforming because it contains a set of compounds that would lead to the formation of benzene during the reforming treatment. These compounds are known by one skilled in the art as being “benzene precursors” and can be, for example, methylcyclopentane, cyclohexane, n-hexane or benzene itself. When the local laws allow it, this intermediate fraction can, however, optionally be sent to the treatment unit of the second intermediate fraction;

- A second intermediate fraction that is desulfurized and denitrated on a conventional hydrotreating catalyst so as to eliminate almost all of the sulfur and the nitrogen initially present in this fraction (i.e., to lower their content to less than 5 ppm, preferably less than 1 ppm). This treatment is accompanied by virtually total hydrogenation of the olefins of this fraction, which makes it possible to lower the olefin content to values that are preferably less than 10% by weight, and more preferably less than 5% by weight. This fraction is then treated on a catalytic reforming catalyst that makes possible the isomerization and the dehydrocyclization of the paraffins and naphthenes with formation of branched paraffins and aromatic compounds.
- The heavy fraction, preferably mixed with the first intermediate fraction, is desulfurized under defined conditions and with a concatenation of catalysts making it possible to reach high desulfurization rates while limiting the hydrogenation rate of the olefins and therefore the octane loss.

Thus, when the light, intermediate and heavy gasoline fractions are mixed after the desulfurization treatments according to the invention, the loss of research octane or engine octane, expressed in the form of the difference between the mean value $(RON+MON)/2$ that is observed in this mixture and the mean value $(RON+MON)/2$ of the initial feedstock, is limited to less than two octane points, preferably less than 1.7 octane points, and more preferably less than 1.5 octane points, and very preferably less than 1 octane point. In some cases, the mean value $(RON+MON)/2$ of the gasoline that is desulfurized with the process according to the invention can even decrease by less than 0.5 octane point relative to the mean value $(RON+MON)/2$ of the feedstock, even, in contrast, increasing by at least 0.5 point.

The sulfur content of the gasoline fractions that are produced by catalytic cracking (FCC) depends on the sulfur content of the feedstock that is treated with FCC, as well as the end point of the fraction. The sulfur contents of the integrality of a gasoline fraction, in particular those that are obtained from FCC, are generally higher than 100 ppm by weight and most times higher than 50 ppm by weight. For gasolines that have end points that are higher than 200°C, the sulfur contents are often higher than 1000 ppm by weight, they can even, in some cases, reach values on the order of 4000 to 5000 ppm by weight.

The process according to the invention pertains in particular when the high desulfurization rates are required, i.e., when the desulfurized gasoline should contain at most 10% of the sulfur of the initial gasoline and optionally at most 5%, even at most 2%, of the sulfur of the initial gasoline, which corresponds to desulfurization rates that are higher than 90%, even higher than 95 or 98%.

The process according to the invention comprises at least the following stages:

a1) At least one stage that consists in running the feedstock that preferably consists of the entire gasoline fraction over a catalyst that makes it possible to hydrogenate selectively the diolefins and the acetylenic compounds of the gasoline without hydrogenating the olefins,

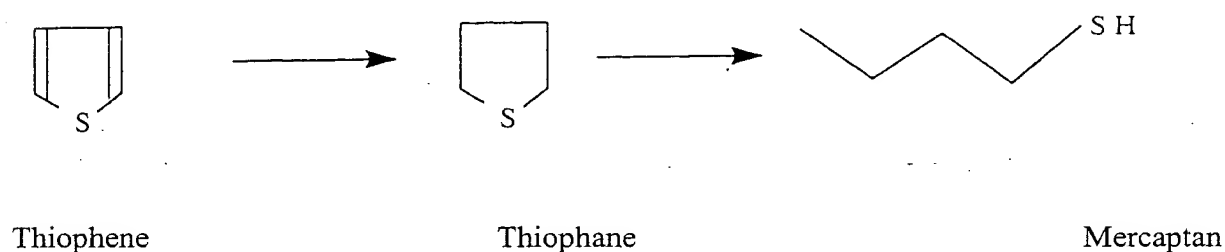
a2) Optionally at least one optional stage that consists in running at least a portion of the initial gasoline or the gasoline hydrogenated in stage a1, preferably the entire initial gasoline or the entire amount of gasoline hydrogenated in stage a1, over a catalyst that makes it possible to transform, at least in part, the light sulfur-containing compounds (for example: ethyl mercaptan, propyl mercaptan, thiophene) with at least a portion of the diolefins or olefins into heavier sulfur-containing compounds. This stage is preferably carried out simultaneously to stage a1 by

running, for example, the initial gasoline over a catalyst that can both hydrogenate the diolefins and acetylenic compounds and transform the light sulfur-containing compounds and a portion of diolefins or olefins into heavier sulfur-containing compounds or over a separate catalyst but that makes it possible to carry out this transformation in the same reactor as stage a1. It is optionally possible to observe on certain types of feedstocks an increase of the mercaptan content at the end of a1) or a2), and this increase of the mercaptan content is probably due to a hydrogenolysis of the disulfides with a high molecular weight. During this stage, all of the light sulfur-containing compounds, i.e., the compounds whose boiling point is less than that of thiophene, can be transformed. It is possible to cite among these compounds the CS₂, the dimethyl sulfide, the methyl ethyl sulfide or COS.

b) At least one stage whose purpose is to separate the initial gasoline into at least one light gasoline (light fraction), at least one intermediate gasoline (intermediate fraction) and a heavy gasoline (heavy fraction). The cutpoint of the light gasoline is determined so as to limit the sulfur content of the light gasoline and to allow its use in the gasoline pool, preferably without any additional treatment, in particular without desulfurization. The cutpoint of the intermediate gasoline is generally conditional upon the restrictions that the reforming process, in which the latter will be treated, imposes. One of the preferred configurations consists in fractionating the gasoline so as to obtain a light fraction, a heavy fraction, and two intermediate fractions: a first intermediate gasoline that primarily consists of compounds with six carbon atoms, which then is preferably mixed with the heavy fraction of the gasoline, preferably before stage c1 or optionally between the saturation treatment of the unsaturated sulfur-containing compounds (stage c1) and the decomposition of these compounds (stage c2), and a second

intermediate gasoline that primarily consists of molecules that contain 7 or 8 carbon atoms (C_7 or C_8) that is treated in stage d.

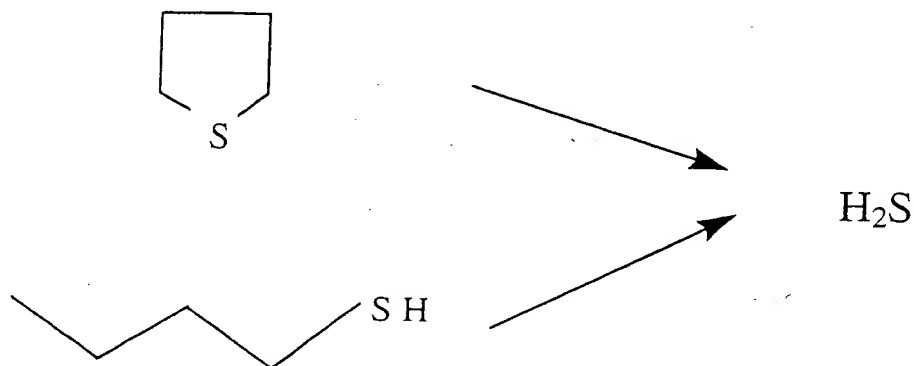
c1) At least one stage that comprises the treatment of at least a portion of the heavy gasoline and optionally at least a portion of the intermediate fractions on a catalyst that makes possible the transformation of at least a portion of the unsaturated sulfur-containing compounds that are present in said feedstock, such as, for example, the thiophenic compounds, into saturated sulfur-containing compounds, such as, for example, the thiophanes (or thiacyclopentanes) or the mercaptans, according to a succession of reactions that are described below:



The total decomposition reaction with release of H_2S is also possible and generally significantly accompanies the saturation reactions of unsaturated, sulfur-containing compounds.

This hydrogenation reaction can be carried out on any catalyst that promotes these reactions, such as, for example, a catalyst that comprises at least one metal of group VIII and/or at least one metal of group VIb, preferably at least in part in sulfide form. When such a catalyst is used, the operating conditions are adjusted so as to be able to hydrogenate at least partly the unsaturated compounds, such as the thiophenic compounds, while limiting the hydrogenation of olefins.

C2) After this treatment, at least one stage c2 optionally may be carried out in which the saturated sulfur-containing compounds that are present in the initial gasoline or that are obtained at the end of the saturation reaction (stage c1) are converted into H_2S according to the examples of reactions:



This treatment can be carried out on any catalyst making possible the conversion of saturated sulfur compounds (primarily the thiophane-type compounds or the mercaptan-type compounds). It may be carried out, for example, on a catalyst that is based on at least one metal of group VIII of the former periodic table (groups 8, 9 or 10 of the new table).

The heavy gasoline that is thus desulfurized is then optionally stripped (i.e., a gas stream, preferably containing one or more cover gases, is run through this gasoline) so as to eliminate the H_2S that is produced during the hydrosulfurization. The light gasoline that is separated in stage b and the heavy gasoline that is desulfurized in stage c1 and/or in stage c2 can then either optionally be mixed and sent into the gasoline pool of the refinery or upgraded separately without

being mixed.

d) The treatment of at least one of the intermediate fractions by a process whose purpose is to eliminate almost all of the sulfur-containing compounds and nitrogen-containing compounds of this fraction, and preferably to hydrogenate all of the olefins, then to treat the thus hydrotreated effluent on a reforming catalyst that makes possible isomerization and dehydrocyclization of the paraffins.

e) Optionally a stage e for mixing at least two fractions of which at least one has undergone a desulfurization treatment in stage c1 and optionally c2 and/or in stage d.

The different stages of the process according to the invention are described in more detail below.

-- Hydrogenation of Diolefins and Acetylenic Compounds (Stage a1):

The hydrogenation of dienes is a stage that makes it possible to eliminate, before hydrodesulfurization, almost all of the dienes that are present in the gasoline fraction that contains sulfur that is to be treated. It takes place preferably in the first stage (stage a1) of the process according to the invention, generally in the presence of a catalyst that comprises at least one metal of group VIII, preferably selected from the group that is formed by platinum, palladium and nickel, and a substrate. For example, a catalyst based on nickel or palladium that is deposited on an inert substrate, such as, for example, alumina, silica or a substrate that contains at least 50% alumina, will be used.

The pressure that is used is adequate for keeping more than 60%, preferably 80%, and more preferably 95% by weight of the gasoline to be treated in liquid phase in the reactor; it is

most generally included between about 0.4 and about 5 MPa and preferably higher than 1 MPa, more preferably between 1 and 4 MPa. The hourly volumetric flow rate of the liquid that is to be treated is between about 1 and about 20 h⁻¹ (volume of feedstock per volume of catalyst and per hour), preferably between 3 and 10 h⁻¹, very preferably between 4 and 8 h⁻¹. The temperature is most generally between about 50 and about 250°C, and preferably between 80 and 230°C, and more preferably between 150 and 200°C, to ensure an adequate conversion of diolefins. Very preferably, it is limited to at most 180°C. The hydrogen to feedstock ratio that is expressed in liters is generally between 5 and 50 liters per liter, preferably between 8 and 30 liters per liter.

The selection of operating conditions is particularly important. The operation will most generally be carried out under pressure and in the presence of an amount of hydrogen that slightly exceeds the stoichiometric value that is necessary for hydrogenating the diolefins and the acetylenic compounds. The hydrogen and the feedstock that is to be treated are injected with an upward flow or a downward flow in a reactor that preferably comprises a fixed catalyst bed.

Another metal can be combined with the main metal to form a bimetallic catalyst, such as, for example, molybdenum or tungsten. The use of such catalytic formulas has been claimed in, for example, Patent FR 2 764 299. The catalytic cracking gasoline can contain up to several % by weight of diolefins. After hydrogenation, the diolefin content is generally reduced to less than 3000 ppm, and even less than 2500 ppm, and more preferably less than 1500 ppm. In some cases, less than 500 ppm can be obtained. The diene content after selective hydrogenation can even, if necessary, be reduced to less than 250 ppm.

According to a particular embodiment of the process according to the invention, the hydrogenation stage of the dienes takes place in a catalytic hydrogenation reactor that comprises

a catalytic reaction zone through which runs the entire feedstock and the amount of hydrogen that is necessary for carrying out the desired reactions.

- Transformation of Light Sulfur Compounds into Heavier Compounds (Stage a2):

This optional stage consists in transforming the light sulfur compounds, which at the end of separation stage b would be found in the light gasoline without this stage. It is preferably carried out on a catalyst that comprises at least one element of group VIII (groups 8, 9 and 10 of the new periodic table), or that comprises a resin. In the presence of this catalyst, the light sulfur compounds are transformed into heavier sulfur-containing compounds, entrained in the heavy gasoline.

This optional stage optionally can be carried out at the same time as stage a1. For example, it can be particularly advantageous to operate, during the hydrogenation of diolefins and acetylenic compounds, under conditions such that at least a portion of the compounds in mercaptan form are transformed. Thus, a certain reduction of the mercaptan content is obtained. To do this, it is possible to use the hydrogenation procedure of the dienes described in Patent Application EP-A-0 832 958, which advantageously uses a catalyst based on palladium, or the one that is described in Patent FR 2 720 754.

Another possibility is to use a catalyst that is based on nickel and that is identical or different from the catalyst of stage a1, such as, for example, the catalyst that is recommended in the process of Patent US-A-3 691 066 that makes it possible to transform the mercaptans (butylmercaptan) into heavier sulfur-containing compounds (methyl thiophene).

Another possibility for carrying out this stage consists in hydrogenating at least in part the

thiophene into thiophane whose boiling point is higher than that of thiophene (boiling point 121°C). This stage can be carried out on a catalyst based on nickel, platinum or palladium. In this case, the temperatures are generally between 100 and 300°C and preferably between 150 and 250°C. The H₂/feedstock ratio is adjusted between 1 and 20 liters per liter, preferably between 2 and 15 liters per liter, for making possible the desired hydrogenation of thiophenic compounds while reducing the hydrogenation of the olefins that are present in the feedstock. The volumetric flow rate is generally between 1 and 10 h⁻¹, preferably between 2 and 4 h⁻¹, and the pressure is between 0.5 and 5 MPa, preferably between 1 and 3 MPa. During this stage, regardless of the process used, a portion of the light sulfur-containing compounds, such as the sulfides (dimethyl sulfide, methyl ethyl sulfide), CS₂, and COS, can also be transformed.

Another possibility for carrying out this stage consists in running the gasoline over a catalyst that has an acidic function that makes it possible to carry out the addition of the sulfur-containing compounds in mercaptan form on the olefins and to carry out the reaction for alkylation of thiophene by these same olefins. It is possible, for example, to run the gasoline that is to be treated over an ion-exchange resin, such as a sulfonic resin. The operating conditions will be adjusted to carry out the desired transformation while limiting the parasitic reactions of oligomerization of the olefins. The operation is generally carried out in the presence of a liquid phase, at a temperature of between 10 and 150°C and preferably between 10 and 70°C. The operating pressure is between 0.1 and 2 MPa and preferably between 0.5 and 1 MPa. The volumetric flow rate is generally between 0.5 and 10 h⁻¹ and preferably between 0.5 and 5 h⁻¹. In this stage, the mercaptan conversion rate is generally higher than 50% and the thiophene transformation rate is generally higher than 20%.

To minimize the oligomerizing activity of the acidic catalyst that is optionally used, a known compound can be used as an additive in gasoline to inhibit the oligomerizing activity of the acid catalysts, such as, for example, the alcohols, the ethers or water.

- **Separation of the Gasoline into At Least Three Fractions (Stage b):**

In this stage, the gasoline is fractionated into at least three fractions:

- A light fraction that has a residual sulfur content that is preferably limited to 50 ppm, more preferably limited to 25 ppm, and very preferably limited to 10 ppm, and that preferably makes it possible to use this fraction without other treatment whose purpose is to reduce its sulfur content,
- At least one intermediate fraction that has an olefin content and an aromatic compound content that are relatively low,
- A heavy fraction in which the majority of the sulfur, initially present in the feedstock, is concentrated.

This separation is carried out preferably with a standard distillation column that is also called a splitter. This fractionation column should make it possible to separate a light fraction from the gasoline that contains a small sulfur fraction, at least one intermediate fraction that consists primarily of compounds that have 6 to 8 carbon atoms, and a heavy fraction that contains the major portion of the sulfur that is initially present in the initial gasoline.

This column generally operates at a pressure of between 0.1 and 2 MPa and preferably between 0.2 and 1 MPa. The number of theoretical plates of this separation column is generally between 10 and 100 and preferably between 20 and 60. The reflux rate of the column that is

expressed by the ratio between the liquid flow rate in the column and the feedstock flow rate is generally less than the unit and preferably less than 0.8, when these flow rates are measured in kilograms per hour (kg/h).

The light gasoline that is obtained at the end of the separation generally contains at least all of the C₅ olefins, preferably the C₅ olefins and at least 20% of the C₆ olefins. Generally, this light fraction has a low sulfur content (for example less than 50 ppm), i.e., it is not in general necessary to treat the light fraction before using it as a fuel. In some extreme cases, however, a softening of the light gasoline can be considered.

- Hydrogenation of the Unsaturated Sulfur Compounds (Stage c1):

This stage, which pertains to the heavy gasoline that is optionally mixed with at least a portion of an intermediate fraction that is obtained at the end of separation stage b). This intermediate fraction preferably essentially consists of (i.e., at more than 60% by weight, preferably more than 80% by weight) C₆ or C₇ molecules as well as the majority of the sulfur-containing compounds that have a boiling point that is close to that of the azeotrope of the thiophene with paraffins, to nearly 20%. This stage consists in transforming at least a portion of the unsaturated sulfur compounds such as the thiophenic compounds, into saturated compounds, for example into thiophanes (or thiacyclopentanes) or into mercaptans, or else optionally to hydrogenolyze at least partially these unsaturated sulfur-containing compounds for forming H₂S.

This stage can, for example, be carried out by passage of the heavy fraction, optionally mixed with at least a portion of an intermediate fraction on a catalyst that comprises at least one element of group VIII and/or at least one element of group VIb at least in part in sulfide form, in

the presence of hydrogen, at a temperature of between about 200°C and about 350°C, and preferably between 220°C and 290°C, under a pressure that is generally between about 1 and about 4 MPa, preferably between 1.5 and 3 MPa. The volumetric flow rate of the liquid is between about 1 and about 20 h⁻¹ (expressed by volume of liquid per volume of catalyst and per hour), preferably between 1 and 10 h⁻¹, very preferably between 3 and 8 h⁻¹. The H₂/HC ratio is between 50 to 600 liters per liter and preferably between 300 and 600 liters per liter.

To carry out, at least in part, the hydrogenation of the unsaturated, sulfur-containing compounds of the gasoline according to the process of the invention, at least one catalyst is generally used that comprises at least one element of group VIII (metals of groups 8, 9 and 10 of the new table, i.e., iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium or platinum) and/or at least one element of group VIb (metals of group 6 of the new table, i.e., chromium, molybdenum, or tungsten) on a suitable substrate.

The metal content of group VIII that is expressed in terms of oxide is generally between 0.5 and 15% by weight, preferably between 1 and 10% by weight. The metal content of group VIb is generally between 1.5 and 60% by weight, preferably between 3 and 50% by weight.

The element of group VIII, when it is present, is preferably cobalt, and the element of group VIb, when it is present, is generally molybdenum or tungsten. Combinations such as cobalt-molybdenum are preferred. The substrate of the catalyst is usually a porous solid, such as, for example, an alumina, a silica-alumina or other porous solids, such as, for example, magnesia, silica, or titanium oxide, alone or mixed with alumina or silica-alumina. To reduce the hydrogenation of olefins that are present in heavy gasoline, it is advantageous to use preferably a catalyst in which the molybdenum density, expressed in % by weight of MoO₃ per unit of surface

area, is higher than 0.07 and preferably higher than 0.10. The catalyst according to the invention preferably has a specific surface area that is less than $190 \text{ m}^2/\text{g}$, more preferably less than $180 \text{ m}^2/\text{g}$ and very preferably less than $150 \text{ m}^2/\text{g}$.

After introduction of the element or elements and optionally shaping of the catalyst (when this stage is carried out on a mixture that already contains the basic elements), the catalyst is in a first activated stage. This activation can correspond either to an oxidation then to a reduction, or to a direct reduction, or to a calcination only. The calcination stage is generally carried out at temperatures of about 100 to about 600°C and preferably between 200 and 450°C , under a flow of air. The reduction stage is carried out under conditions that make it possible to convert at least a portion of the oxidized forms of the metal of group VIII and/or group VIb to the metallic state. Generally, it consists in treating the catalyst under a flow of hydrogen at a temperature that is preferably at least equal to 300°C . The reduction can also be carried out in part with chemical reducing agents.

The catalyst is preferably used at least in part in its sulfurized form. The introduction of sulfur can take place before or after any activation stage, i.e., calcination stage or reduction stage. Preferably, no oxidation stage is carried out after the sulfur or a sulfur-containing compound has been introduced on the catalyst. It is therefore preferable, for example, when the catalyst is sulfurized after drying not to calcinate the catalyst; in contrast, a reduction stage optionally can be carried out after the sulfurization.

The sulfur or a sulfur-containing compound can be introduced *ex situ*, i.e., outside of the reactor where the process according to the invention is carried out, or *in situ*, i.e., in the reactor that is used for the process according to the invention. In the latter case, the catalyst is preferably

reduced under the conditions that are described above, then sulfurized by passage of a feedstock that contains at least one sulfur-containing compound, which once decomposed leads to the attachment of sulfur to the catalyst. This feedstock can be gaseous or liquid, for example hydrogen that contains H_2S , or a liquid that contains at least one sulfur-containing compound.

In a preferred way, the sulfur-containing compound is added to the catalyst *ex situ*. For example, after the calcination stage, a sulfur-containing compound can be introduced on the catalyst optionally in the presence of another compound. The catalyst is then dried, then transferred into the reactor that is used to implement the process according to the invention. In this reactor, the catalyst is then treated under hydrogen so as to transform at least a portion of the main metal into sulfide. A procedure that is particularly suited to the invention is the one that is described in Patents FR-B- 2 708 596 and FR-B-2 708 597.

In the process according to the invention, the conversion of the unsaturated sulfur-containing compounds is higher than 15% and preferably higher than 50%. In the same step, the hydrogenation rate of the olefins is preferably less than 50%, more preferably less than 40%, and very preferably less than 35% during this stage.

In the process according to the invention, the treated gasoline in stage c1 optionally can contain at least a portion of at least one intermediate fraction that is obtained in stage b. For example, it may be advantageous to treat in this stage a fraction of the gasoline that it is not desirable to send in the catalytic reforming process.

The effluent that is obtained from this first hydrogenation stage is optionally then sent to stage c2 that makes it possible to decompose the H_2S -saturated sulfur-containing compounds.

- Decomposition of the Saturated Sulfur Compounds (Stage c2):

The feedstock of this stage consists of either only the effluent that is obtained from stage c1 or a mixture that comprises the effluent of stage c1 and at least a portion of at least one intermediate fraction. This intermediate fraction preferably essentially consists of (i.e., with more than 60% by weight, preferably more than 80% by weight) C₆ or C₇ molecules as well as the largest portion of the sulfur-containing compounds that have a boiling point that is close to that of the azeotrope of the thiophene with hydrocarbons at nearly 20%.

In this stage, the saturated sulfur compounds are transformed in the presence of hydrogen on a suitable catalyst. The decomposition of the unsaturated compounds that are not hydrogenated during stage c1 can also take place simultaneously. This transformation is carried out without significant hydrogenation of the olefins, i.e., during this stage, the amount of hydrogenated olefins is generally limited to less than 20% by volume relative to the olefin content of the initial gasoline and preferably limited to 10% by volume relative to the olefin content of the initial gasoline.

The catalysts that may be suitable to this stage of the process according to the invention, without this list being limiting, are catalysts that generally comprise at least one basic element (metal) that is selected from among the elements of group VIII, and preferably selected from the group that is formed by nickel, cobalt, iron, molybdenum, and tungsten. These metals can be used alone or in combination; they are preferably supported and used in their sulfurized form. It is also possible to add at least one promoter to these metals, for example tin. Preferably catalysts that comprise nickel, or nickel and tin, or nickel and iron, or cobalt and iron, or else cobalt and tungsten, will be used. Said catalysts are more preferably sulfurized, and very preferably

presulfurized in-situ or ex-situ. The catalyst of stage 2 preferably has a nature and/or composition that is different from the one that is used in stage c1.

The base metal content of the catalyst according to the invention is generally between about 1 and about 60% by weight, preferably between 5 and 20% by weight, and very preferably between 5 and 9% by weight. The catalyst is preferably generally worked into the shape of balls, pellets, or extrudates, for example trilobes. The metal can be incorporated in the catalyst by deposition on the preformed substrate. It can also be mixed with the substrate before the shaping stage. The metal is generally introduced in the form of a precursor salt, generally water-soluble, such as, for example, nitrates and heptamolybdates. This method of introduction is not specific to the invention. Any other method of introduction that is known to one skilled in the art may be suitable.

The substrates of the catalysts that are used in this stage of the process according to the invention are generally porous solids that are selected from among the refractory oxides, such as, for example, the aluminas, the silicas, and the silica-aluminas, magnesia, as well as titanium oxide and zinc oxide, whereby these last oxides can be used by themselves or mixed with alumina or silica-alumina. The substrates are preferably transition aluminas or silicas whose specific surface area is between 25 and 350 m²/g. The natural compounds, such as, for example, diatomaceous earth or kaolin, can also be suitable as substrates of catalysts that are used in this stage of the process.

According to a preferred method of preparation of the catalyst, after introduction of at least one metal or precursor of said metal and optionally shaping of the catalyst, the catalyst is in a first activated stage. This activation can correspond either to an oxidation, then to a reduction,

or to a reduction after drying without calcination, or else only to a calcination. The calcination stage when it is present is generally carried out at temperatures from about 100°C to about 600°C and preferably between 200°C and 450°C, under a flow of air. The reduction stage is carried out under conditions that make it possible to convert at least a portion of the oxidized forms of the base metal to the metallic stage. Generally, it consists in treating the catalyst under a flow of hydrogen at a temperature that is at least equal to 300°C. The reduction can also be carried out in part by means of chemical reducing agents.

The catalyst is preferably used at least in part in its sulfurized form, which exhibits the advantage of limiting to the maximum the hydrogenation risks of the unsaturated compounds, such as the olefins or the aromatic compounds, during the start-up phase. The introduction of sulfur can take place between different activation stages. Preferably, no oxidation stage is carried out when the sulfur or a sulfur-containing compound has been introduced on the catalyst. The sulfur or a sulfur-containing compound can be introduced *ex situ*, i.e., outside of the reactor where the process according to the invention is carried out, or *in situ*, i.e., in the reactor that is used for the process according to the invention. In the latter case, the catalyst is preferably reduced under the conditions that are described above, then presulfurized by passage of a feedstock that contains at least one sulfur-containing compound, which once decomposed leads to the attachment of sulfur to the catalyst. This feedstock can be gaseous or liquid, for example hydrogen that contains H₂S or a liquid that contains at least one sulfur-containing compound.

In a preferred way, the sulfur-containing compound is added to the catalyst *ex situ*. For example, after the calcination stage, a sulfur-containing compound can be introduced on the catalyst optionally in the presence of another compound. The catalyst is then optionally dried,

then transferred into the reactor that is used to implement the process of the invention. In this reactor, the catalyst is then treated under hydrogen so as to transform at least a portion of the base metal and optionally another metal into sulfide. A procedure that is particularly suitable to the invention is the one that is described in Patents FR-B- 2 708 596 and FR-B- 2 708 597.

After sulfurization, the sulfur content of the catalyst is in general between 0.5 and 25% by weight, preferably between 4 and 20% by weight, and very preferably between 4 and 10% by weight. The hydrodesulfurization that is carried out during this stage c2 has as its object to convert into H_2S the saturated sulfur-containing compounds of the gasoline that have already undergone at least one previous hydrogenation of the unsaturated sulfur compounds during stage c1. It makes it possible to obtain an effluent that meets the specifications that are desired in terms of content of sulfur-containing compounds. The gasoline that is thus obtained has only a small octane loss (reduction of the research octane number and/or engine octane number).

The treatment whose purpose is to decompose the saturated sulfur-containing compounds obtained from stage c1 of the process is carried out in the presence of hydrogen, with a catalyst that comprises at least one base metal that is selected from the group that is formed by nickel, cobalt, iron, molybdenum, and tungsten, used by themselves or mixed with one another, at a temperature of between about 100°C and about 400°C, preferably between about 150°C and about 380°C, more preferably between 210°C and 360°C, and very preferably between 220°C and 350°C, under a pressure that is generally between about 0.5 and about 5 MPa, preferably between 1 and 3 MPa, more preferably between 1.5 and 3 MPa. The volumetric flow rate of the liquid is between about 0.5 and about 10 h^{-1} (expressed in terms of liquid volume per volume of catalyst and per hour), preferably between 1 and 8 h^{-1} . The H_2/HC ratio is adjusted based on the

desired hydrodesulfurization rates in the range between about 100 and about 600 liters per liter, preferably between 20 and 300 liters per liter. All or part of this hydrogen optionally can be obtained from stage c1 (unconverted hydrogen) or a recycling of unconsumed hydrogen in stages a1, a2, c2 or d.

It has been found that the use of this second catalyst in this stage, under particular operating conditions, makes it possible to decompose the saturated compounds that are contained in the effluent that is obtained from stage c1 into H₂S. This implementation makes it possible to reach a high overall level of hydrodesulfurization at the end of the set of stages of the process according to the invention while reducing the octane loss that results from the saturation of the olefins, because the conversion of the olefins during stage c1 is generally limited to at most 20% by volume of olefins, preferably at most 10% by volume.

- Hydrotreatment of At Least One Intermediate Fraction (Stage d):

The purpose of this treatment of at least one of the intermediate fractions is to eliminate almost all of the sulfur-containing compounds and nitrogen-containing compounds of this fraction and to treat the thus hydrotreated effluent on a reforming catalyst that makes possible the isomerization and the dehydrocyclization of the paraffins. This stage pertains to at least a portion of an intermediate fraction that is obtained in stage b.

It consists in treating said fraction on a catalyst or a group of catalysts making it possible to desulfurize and denitrate totally the fraction that is being considered, i.e., to obtain a fraction that contains a sulfur content and a nitrogen content that is preferably less than 5 ppm, and more preferably less than 1 ppm by weight, by transformation of the sulfur-containing compounds or

nitrogen-containing compounds respectively into H_2S and ammonia.

This stage is generally carried out by running the fraction over at least one conventional hydrotreating catalyst under conditions that make it possible to eliminate sulfur and nitrogen. The catalysts that are particularly suitable are, for example, catalysts that are based on a metal of group VIII such as cobalt or nickel and a metal of group VI, such as tungsten or molybdenum. Typically, without these conditions being limiting, this treatment can be carried out on an HR 306-type or HR448-type catalyst that is marketed by the Procatalyse Company at a temperature of generally between 250 and 350°C, an operating pressure that is generally between 1 and 5 MPa, preferably between 2 and 4 MPa, and a volumetric flow rate that is generally between 2 and 8 h^{-1} (expressed in terms of volume of liquid feedstock per volume of catalyst and per hour). During this treatment, almost all of the olefins that are present in this fraction are hydrogenated.

The effluent that is thus obtained is cooled, and the decomposition products are then separated with any technique that is known to one skilled in the art. It is possible, for example, to cite washing processes, stripping processes or else extraction processes.

The effluent corresponding to one of the desulfurized and denitrated intermediate fractions is then treated on a catalyst or a catalyst concatenation making possible the reforming of said fraction, i.e., to carry out at least in part the dehydrogenation of the saturated cyclic compounds, the isomerization of the paraffins and the dehydrocyclization of the paraffins that are present in the treated intermediate fraction. The purpose of this treatment is to increase the octane number of the fraction that is being considered. This treatment takes place with a standard catalytic reforming process. To do this, it may be advantageous to use, for example, so-called “fixed-bed” or “moving-bed” processes, i.e., processes in which the catalyst is respectively

placed in a fixed bed, or in contrast, a fluidized bed, and optionally circulated in at least one reactor and in an outside circulation loop that optionally comprises other reactors and/or at least one regenerator. In the process that is used, the desulfurized effluent is brought into contact with a reforming catalyst, generally with a platinum base supported on alumina, at a temperature of between 400°C and 700°C, with an hourly volumetric flow rate (kg of treated feedstock per hour and per kg of catalyst) of between 0.1 and 10. The operating pressure can be between 0.1 and 4 MPa. A portion of the hydrogen that is produced during the different reactions can be recycled in a ratio of between 0.1 and 10 mol of hydrogen per mol of feedstock.

Figure 1 presents an embodiment of the process according to the invention. In this example, a gasoline fraction (initial gasoline) that contains sulfur is introduced via pipe 1 into a catalytic hydrogenation reactor 2, which makes it possible to hydrogenate selectively the diolefins and/or the acetylenic compounds that are present in said gasoline fraction (stage a1 of the process). Effluent 3 of the hydrogenation reactor is sent into a reactor 4, which comprises a catalyst that can carry out the transformation of the light sulfur-containing compounds with diolefins or olefins into heavier sulfur-containing compounds (stage a2). Effluent 5 of reactor 4 is then sent to fractionation column 6, which makes it possible to carry out a separation of the gasoline into 3 fractions (stage b).

The first fraction that is obtained is a light fraction 7. This light fraction preferably comprises less than 50 ppm of sulfur and does not require desulfurization, since the light sulfur-containing compounds that are present in the initial gasoline have been transformed into heavier compounds in stage a1.

A second fraction 8 (intermediate fraction) is obtained that is first sent to a catalytic

desulfurization reactor 10, then via line 11 to a catalytic reforming reactor (stage d).

A third fraction (heavy fraction) is obtained via line 9. This fraction is first treated in a reactor 14 on a catalyst that makes it possible to transform at least a portion of the unsaturated sulfur-containing compounds that are present in the feedstock into saturated sulfur-containing compounds (stage c1). Effluent 15 of reactor 14 is sent to a reactor 16 (stage c2) that contains a catalyst that promotes the decomposition into H_2S of saturated sulfur-containing compounds that are initially present in the feedstock and/or formed in reactor 14.

Light fraction 7 as well as effluent 13 (obtained from reforming reactor 14) and effluent 17 (obtained from decomposition reactor 13) are mixed to form desulfurized gasoline 18 (stage e).

According to other preferred embodiments, presented in Figure 1, it is also possible to send at least a portion of the non-desulfurized intermediate fraction (line 8) either via line 19 then mixed with heavy fraction 9 to reactor 14 (stage c1) or via line 20 then mixed with effluent 15 to reactor 16 (stage c2).

The following examples illustrate the invention.

Example 1 (For Comparison)

A catalytic cracking gasoline whose characteristics are grouped in Table 1 is treated for the purpose of reaching a specification of the gasoline pool at the outlet of the refinery such that the sulfur content is less than 10 ppm, which requires reducing the sulfur content of a gasoline that is obtained from a catalytic cracking unit with less than 20 ppm by weight.

The gasoline is separated into three fractions: a light fraction whose distillation interval

is between 35°C and 95°C, an intermediate fraction whose distillation interval is between 95°C and 150°C, and a heavy fraction whose distillation interval is between 150°C and 250°C.

The sulfur content of the light gasoline, which represents 38% by volume of the total gasoline, is 210 ppm by weight.

The intermediate and heavy fractions are treated on an HR306 catalyst of the Procatalyse Company. The catalyst (20 ml) is first sulfurized by treatment for 4 hours under a pressure of 3.4 MPa at 350°C, upon contact with a feedstock that consists of 2% sulfur in dimethyl disulfide form in n-heptane. The desulfurization stage is carried out at 300°C under 35 bar with an H₂/HC of 150 l/l and a VVh of 3 h⁻¹. Under these treatment conditions, the effluents that are obtained after stripping of H₂S contain 1 ppm of sulfur. The mixture of these two desulfurized fractions with the lightest fraction leads to a gasoline that contains 81 ppm by weight of sulfur.

Table 1

Sulfur (ppm by weight)	2000		
Olefins (% by volume)	30		
Aromatic Compounds (% by volume)	40		
Paraffin + Naphthenes (% by volume)	30		
RON	91.0		
MON	81.1		
Density	0.77		
	Distillation		
% Distilled Volume	Boiling Point (°C)	Sulfur (% of cumulative weight)	Olefins (% of cumulative weight)
0	35	0	0
10	55	0.8	21
30	85	2.1	52

50	120	7.5	77
70	155	20	92
90	200	49	99
100	240	100	100

Example 2:

The gasoline that is obtained from a catalytic cracking unit whose characteristics are described in Example 1 is subjected to a hydrogenation treatment of the diolefins under conditions where the light sulfur-containing compounds that are present in the feedstock are partly converted into heavier compounds (simultaneous stages a1 and a2).

This treatment is carried out in a reactor that operates continuously and in upward flow. The catalyst is based on nickel and molybdenum (HR945 catalyst marketed by the Procatalyse Company). The catalysts are first sulfurized by treatment for 4 hours under a pressure of 3.4 MPa at 350°C, upon contact with a feedstock that consists of 2% sulfur in dimethyl disulfide form in n-heptane. The reaction is conducted at 160°C under a total pressure of 1.3 MPa, with a volumetric flow rate of 6 h⁻¹. The H₂/feedstock ratio, expressed in liter of hydrogen per liter of feedstock, is 10.

The gasoline is then separated into two fractions, whereby one has a distillation interval between 35°C and 80°C and represents 29% by volume, and the other distills between 80°C and 240°C and represents 71% by volume of the gasoline fraction. The sulfur content of the light gasoline is 22 ppm by weight.

The heavy gasoline is subjected to a hydrodesulfurization on a concatenation of catalysts in an isothermal tubular reactor. The first catalyst (catalyst A, stage c1) is obtained by impregnation “without excess solution” of a transition alumina that comes in ball form with a specific surface area of 130 m²/g and a pore volume of 0.9 ml/g, by an aqueous solution that contains molybdenum and cobalt in the form of ammonium heptamolybdate and cobalt nitrate. The catalyst is then dried and calcined under air at 500°C. The content of cobalt and molybdenum of this sample is 3% of CoO and 10% of MoO₃.

The second catalyst (catalyst B, stage c2) is prepared from a transition alumina of 140 m²/g that comes in the form of balls that are 2 mm in diameter. The pore volume is 1 ml/g of substrate. 1 kilogram of substrate is impregnated by 1 liter of nickel nitrate solution. The catalyst is then dried at 120°C and calcined under a stream of air at 400°C for one hour. The nickel content of the catalyst is 20% by weight.

25 ml of catalyst A and 50 ml of catalyst B are placed in the same hydrodesulfurization reactor such that the feedstock that is to be treated (heavy fraction) first meets catalyst A (stage c1) then catalyst B (stage c2). A zone for sampling the effluent that is obtained from stage c1 is provided between catalysts A and B. The catalysts are first sulfurized by treatment for 4 hours under a pressure of 3.4 MPa at 350°C, upon contact with a feedstock that consists of 2% sulfur in dimethyl disulfide form in n-heptane.

The operating conditions of the hydrodesulfurization are as follows: $VVH = 1.33 \text{ h}^{-1}$ relative to the entire catalytic bed $H_2/HC = 360 \text{ l/l}$, $P = 1.8 \text{ MPa}$. The temperature of the catalytic zone that comprises catalyst A is 260°C, and the temperature of the catalytic zone that contains catalyst B is 350°C. The product that is obtained contains 19 ppm of sulfur.

The desulfurized product is recombined with light gasoline. The measurement of the sulfur content of the gasoline that is thus obtained leads to a content of 20 ppm by weight. It has a RON of 88.1 and a MON of 79.6 or a loss of $(RON + MON)/2$ of 2.2 points relative to the feedstock. The olefin content of this gasoline is 22% by volume.

Example 3 (According to the Invention):

The gasoline that is obtained from a catalytic cracking unit whose characteristics are described in Example 1 is subjected to a hydrogenation treatment of the diolefins under conditions where the light sulfur-containing compounds that are present in the feedstock are partly converted into heavier compounds (simultaneous stages a1 and a2).

This treatment is carried out in a reactor that operates continuously and in upward flow. The catalyst is based on nickel and molybdenum (HR945 catalyst marketed by the Procatalyse Company). The catalysts are first sulfurized by treatment for 4 hours under a pressure of 3.4 MPa at 350°C, upon contact with a feedstock that consists of 2% sulfur in dimethyl disulfide form in n-heptane. The reaction is conducted at 160°C under a total pressure of 1.3 MPa with a volumetric flow rate of 6 h^{-1} . The $\text{H}_2/\text{feedstock}$ ratio, expressed in liter of hydrogen per liter of feedstock, is 10.

The gasoline is then separated into four fractions:

- One having a distillation interval of between 35°C and 80°C and representing 28% by volume and having a sulfur content of 20 ppm by weight;
- A second fraction distilling between 80°C and 95°C and representing 10% by volume of the initial gasoline and containing 250 ppm by weight of sulfur;

- A third fraction distilling between 95°C and 150°C, representing 30% by volume of the initial gasoline and containing 1000 ppm by weight of sulfur. The RON and the MON of this fraction are respectively 90 and 79.
- A fourth fraction distilling between 150°C and 240°C, representing 32% by volume of the initial gasoline and containing 4600 ppm by weight of sulfur.

The heavy gasoline is mixed with the second fraction and is subjected to a hydrodesulfurization on a concatenation of catalysts in an isothermal tubular reactor. The first catalyst (catalyst A, stage c) is obtained by impregnation “without excess solution” of a transition alumina that comes in the form of balls with a specific surface area of 130 m²/g and a pore volume of 0.9 ml/g, by an aqueous solution that contains molybdenum and cobalt in ammonium heptamolybdate form and cobalt nitrate form. The catalyst is then dried and calcined under air at 500°C. The cobalt and molybdenum content of this sample is 3% of CoO and 10% of MoO₃.

The second catalyst (catalyst B, stage d) is prepared from a transition alumina of 140 m²/g that comes in the form of balls with a diameter of 2 mm. The pore volume is 1 ml/g of substrate. 1 kilogram of substrate is impregnated by 1 liter of nickel nitrate solution. The catalyst is then dried at 120°C and calcined under a stream of air at 400°C for one hour. The nickel content of the catalyst is 20% by weight.

25 ml of catalyst A and 50 ml of catalyst B are placed in the same hydrodesulfurization reactor so that the feedstock that is to be treated (heavy fraction) first meets catalyst A (stage c) and then catalyst B (stage d). A zone for sampling the effluent that is obtained from stage c is provided between catalysts A and B. The catalysts are first sulfurized by treatment for 4 hours under a pressure of 3.4 MPa at 350°C, upon contact with a feedstock that consists of 2% sulfur in

dimethyl disulfide form in n-heptane.

The operating conditions of the hydrodesulfurization are as follows: $VVH = 1.33 \text{ h}^{-1}$ relative to the entire catalyst bed $H_2/HC = 360 \text{ l/l}$, $P = 1.8 \text{ MPa}$. The temperature of the catalytic zone that comprises catalyst A is 260°C , and the temperature of the catalyst zone that contains catalyst B is 350°C . The product that is obtained contains 37 ppm of sulfur.

The third fraction is treated on an HR306 catalyst of the Procatalyse Company. The catalyst (20 ml) is first sulfurized by treatment for 4 hours under a pressure of 3.4 MPa at 350°C , upon contact with a feedstock that consists of 2% of sulfur in dimethyl disulfide form in n-heptane. The desulfurization stage is carried out at 300°C under 3.5 MPa with an $H_2/H C$ of 150 l/l and a VVH of 3 h^{-1} . Under these treatment conditions, the effluent that is obtained after the stripping of H_2S contains less than 1 ppm of sulfur. The olefin content is 0.9% by volume and the octane values are 68.7 for the RON and 68.3 for the MON. The gasoline that is obtained is then treated on a reforming catalyst CR201 that is marketed by the Procatalyse Company. The catalyst (30 ml) is first reduced to 500°C under a stream of hydrogen before use. The reforming treatment is carried out at 470°C under a pressure of 7 bar. The H_2/HC ratio is 500 l/l. The VVH is 2 h^{-1} .

The effluent is stabilized by elimination of the compounds that have less than 5 carbon atoms. The reformate that is obtained, which represents 86% of the fraction of the treated gasoline, has a sulfur content that is less than 1 ppm by weight, a RON of 97 and a MON of 86.

The fractions that are obtained from different treated fractions are remixed. The sulfur content is 20 ppm by weight. The mean value $(RON+MON)/2$ of the total desulfurized gasoline increased by 1.3 points relative to that of the initial gasoline. In addition, the hydrogen that is

produced during the catalytic reforming stage can be used for the hydrotreatment reaction sections, which is an obvious advantage of the process.

CLAIMS

1. Process for the production of gasoline with a low sulfur content from a feedstock that contains sulfur, comprising at least the following stages:

a1) at least one selective hydrogenation of diolefins and acetylenic compounds that are contained in the feedstock,

b) At least one separation of the effluent that is obtained at the end of stage a1 into at least three fractions: a light fraction that is virtually lacking sulfur and that contains the lightest olefins, a heavy fraction in which the major portion of the sulfur-containing compounds that are initially present in the initial gasoline is concentrated, and at least one intermediate fraction that has relatively low contents of olefins and aromatic compounds,

c1) At least one treatment of the heavy gasoline that is separated in stage b on a catalyst that makes it possible to decompose or to hydrogenate at least partially the unsaturated sulfur-containing compounds,

d) At least one stage for desulfurization and denitration of at least one intermediate fraction, followed by a catalytic reforming.

2. Process according to claim 1 that also comprises at least one stage a2 that is located before stage b and whose purpose is to increase the molecular weight of the light sulfur-containing products that are present in the feedstock and/or the effluent of stage a1.

3. Process according to one of claims 1 or 2 that also comprises a stage c2 for treatment of the effluent of stage c1 on a catalyst that makes it possible to decompose the sulfur-containing compounds.

4. Process according to claim 3, wherein the catalyst of stage c2 also makes it possible to limit the hydrogenation of the olefins to less than 20% by volume.
5. Process according to any of claims 1 to 4 that also comprises a stage e for mixing at least two fraction of which at least one has been desulfurized in stage c1 and optionally c2 and/or in stage d.
6. Process according to any of claims 1 to 5, wherein a portion of at least one intermediate fraction that is obtained in stage b is mixed with the heavy fraction that is obtained from stage b before stage c1.
7. Process according to any of claims 1 to 5, wherein a portion of at least one intermediate fraction that is obtained in stage b is mixed with the effluent of stage c1.
8. Process according to any of claims 1 to 7, wherein stage d for desulfurization and denitration is accompanied by a total hydrogenation of olefins.
9. Process according to any of claims 1 to 8, wherein the feedstock is a gasoline fraction that is obtained from a catalyst cracking unit.
10. Process according to any of claims 1 to 9, wherein stage b comprises a separation of the effluent that is obtained at the end of stage a1 into four fractions: a light fraction, a heavy fraction, and two intermediate fractions, and wherein one of the intermediate fractions is treated in stage d and the other is mixed with the heavy fraction that is separated in stage b and then treated in stage c1.